SERPENTINE-FUSED PHOSPHATE

Citric Solubility and Glass Content Correlation

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Olivine and serpentine have been used successfully in plant scale operations for solubilizing the phosphorus pentoxide in phosphate rock. Among the properties of the new phosphate material so far reported, most interesting is its amorphous nature which is closely related to its chemical as well as argonomic availability. A study of the correlation between the availability of the fused material and its amorphous nature may yield results of practical interest.

OLIVINE AND SERPENTINE have been used successfully in plant scale operations for solubilizing the phosphorus pentoxide in phosphate rock (7-11, 15-17, 20) since the publication in 1943 of an article by Walthall and Bridger describing the magnesium silicate fusion process (20, 21). Among the properties of this new phosphate material so far reported, most interesting is its amorphous nature which is closely related to its chemical as well as agronomic availability (3, 4, 7, 14, 20). [The amorphous nature of this type of fused phosphate was first mentioned in a German patent granted in 1939 to Schleede and associates (19).] However, a detailed knowledge of the correlation between the availability of the fused material and its amorphous nature is lacking. A study of the correlation, it is believed, might yield results of practical interest.

Materials and Method

Samples Available Samples of the XS and LS series (Table I) were laboratory preparations obtained by fusing Christmas Island and Laokay (formerly of Indo-China) phosphates with Taiwan serpentine in a small arc furnace (10, 11). The effect of varying the proportions of serpentine to the phosphates used is well demonstrated. The color of the products ranged from dirty green through light green to greenish gray, but all appeared pale green when pulverized.

It has been reported that finer quenched products exhibit a higher solubility (8, 11). Results of solubility tests on the mechanical separates of a random sample are shown in Table II. Samples of the I-23-S series were obtained from stockpile I-23.

Samples of the I and II series (Table III) were pilot plant products (11). Most of them were bluish black in color and had a metallic luster. All were obtained by fusing Florida pebble phosphate with Taiwan serpentine in a 1200-kw. arc resistance furnace using Soderberg electrodes. Samples of the PS series were products of regular plant-scale operation, in which both Soderberg and baked carbon electrodes were used. These had a dirty green color; all appeared light gray or greenish gray when pulverized.

Table I. Effect of Varying Proportions of Serpentine to High- and Low-Fluorine Phosphate Rocks on Citric Solubility and Glass Content of Fused Products

Sample No.	Weight Ratio of Phosphate Rock to Serpentine	Citric Solubility[a], %	Glass Content, %
XS3[b]	10:3	47	7.5
XS4	10:4	63	33.0
XS5	10:5	77	75.0
XS6	10:6	79	71.0
XS7	10:7	84	84.0
XS8	10:8	87	86.0
LS3[c]	10:3	37	18.0
LS4	10:4	62	67.0
LS5	10:5	86	77.5
LS6	10:6	93	89.3
LS7	10:7	89	81.5
LS8	10:8	93	88.8

[a] All determinations made on −100-mesh samples.

[b] Christmas Island phosphate containing 39.0% P_2O_5 and 0.8% F, fused with Taiwan serpentine.

[c] Laokay phosphate containing 32.7% P_2O_5 and 2.7% F.

A total of 83 samples from pilot and plant scale operations were available, only 16 of which are shown in Table III. Sample C was removed from the furnace hearth during repair. It was bluish gray in color and had a limestonelike fracture. This represented a completely reverted fused phosphate.

Preparation of Low - Analysis Samples by Heat Treatment Previous studies have demonstrated that serpentine - fused phosphate might show serious reduction in citric solubility when heated at 700° or 800° for 2 hours or 600° C. for 6 hours (11) (Figure 1). The effect of heat treatment on the solubility of a sample of plant scale product as shown in Figure 2 is typical of most of the Florida pebble phosphate–Taiwan serpentine-fused glasses when subjected to heat treatment at shorter periods.

Most of the samples described had a high citric solubility. To obtain more low-analysis samples in order to facilitate a better understanding of the correlation, four large samples were taken from stockpiles I-6, I-19, PS, and TP; the latter was imported Thermo-Phos Granular marketed by the Permanente Metals Corp. of California. Table IV shows the partial analysis of the four stock samples. The TP material, very different from the producer's experimental products, appeared as a dark gray granular material spotted with white grains. These were all ground to pass a 20-mesh screen to minimize sampling error, thoroughly mixed, heated in 20-gram portions at 300°, 500°, 700°, and 880° C. for 2, 4, 6, and 8 hours, and then quenched in water. Some other heat-treatment tests were carried out at other temperatures for

Table II. Effect of Particle Size of Quenched Product on Citric Solubility and Glass Content

Sample No.	Size, Mesh, Tyler Standard	Weight, % of Total	Citric Solubility[a], %	Glass Content, %
..	+4	0.93	47.5	..
..	−4, +8	7.10	59.8	..
..	−8, +14	28.80	81.9	..
..	−14, +28	37.50	89.2	..
..	−28, +48	19.40	87.9	..
..	−48, +100	4.80	87.1	..
..	−100	1.30	87.5	..
I-23-S1[b]	+10	..	77.8	71.0
I-23-S2[b]	−10, +32	..	67.9	68.5
I-23-S3[b]	−32, +48	..	98.9	96.8
I-23-S4[b]	−48	..	96.3	95.9

[a] All determinations made on −100-mesh samples.
[b] Mechanical separates of random sample from stockpile I-23.

Table III. Citric Solubility and Glass Content of Some Pilot and Plant Scale Products

Sample No.	Size of Phosphate Rock[a] Used	Kind of Serpentine Used	Citric Solubility[b], %	Glass Content, %
I-5	+10-mesh	Raw	60.5	75.0
I-10	+10-mesh	Raw	97.7	85.8
I-15	+10-mesh	Raw	93.8	94.2
I-20	+10-mesh	Raw	90.5	95.2
I-25	+10-mesh	Raw	91.5	90.0
I-30	+10-mesh	Raw	83.4	93.8
II-5	Run-of-mine	Raw	95.5	93.5
II-10	Run-of-mine	Raw	90.8	97.5
II-15	Run-of-mine	Raw	92.0	96.6
II-20	Run-of-mine	Calcined	96.4	93.8
II-25	Run-of-mine	Calcined	96.2	81.0
II-30	Run-of-mine	Calcined	93.6	84.5
II-35	Run-of-mine	Calcined	78.2	90.5
PS-5	Run-of-mine	Raw	99.2	84.5
PS-10	Run-of-mine	Raw	97.3	92.3
PS-15	Run-of-mine	Raw	96.2	90.0
C			12.7	0

[a] Florida pebble phosphate.
[b] All determinations made on −100-mesh samples.

various lengths of time and in different manners. A total of 58 samples of the A series were obtained. The selected results shown in Table V are typical.

A total of 165 samples were available for petrographical studies.

Determination of Citric Solubility In spite of the resolution made by the Association of Official Agricultural Chemists in October 1949 to replace the 2% citric acid test for basic slag with that using neutral ammonium citrate (12), it is believed that Wagner's test, being comparatively simpler, would still serve as a reliable measure of the relative plant-food value of basic slag. This test, which has been used in previous studies with phosphate rock–magnesium silicate glasses (4, 7, 8, 10, 15–17, 19, 20) and also with raw phosphates (5, 6), is the official method now in use in Japan and China for evaluation of the fertilizer efficiency of serpentine-fused phosphate.

The 165 samples were dried at about 105° C., all ground to pass a 100-mesh screen, Tyler standard, and analyzed for total and citric-soluble phosphorus pen-

toxide according to the former AOAC standard procedure for basic slag (1).

Examination with Polarizing Microscope Petrographical examinations were made with a Leitz polarizing microscope in the laboratory of the Taiwan Geological Survey (22). Magnifications of 26× and 80× were used for fractured coarse and finely ground samples, respectively.

The percentage of the observed grains which became dark between crossed Nicol prisms and in all positions of rotation of the stage was estimated, giving results which differed mostly in 5% units. The slide was shifted to cover new fields and a total of 10 observations were made. The preparation and examination of each sample could be completed in 5 to 10 minutes.

Results and Discussion

Physical and Chemical Changes as a Result of Heat Treatment The first remarkable change as a result of heat treatment is that of color. Serpentine-fused phosphates showed substantially no color changes at 300° or 500° C. after 8 hours' treatment. When heated at 700° and 880° C., obvious changes were observed, but different samples followed very different patterns. Sample I-6, which was one of low conversion, appeared dull purplish black after 2 hours' heating at 700° C.; when the time of heat treatment was increased through 4 and 6 to 8 hours, the color appeared lighter and finally became dull brasslike. The PS sample lost its dirty green slight transparent appearance and became bluish black with metallic luster after 2 hours' heating at 700° C. After longer treatment at the same temperature, both I-19 and PS gained in brightness and finally all had a bright pyritelike appearance after 8 hours' heating. Under similar treatments, the gray TP sample became paler and was finally turned into a mass of dull sandlike grains. At 880° C., similar but more rapid changes took place. After .8 hours' heating the I-6 and TP samples all became mixtures of dull sandlike grains, while the I-19 and PS samples still retained some of the pyritelike metallic luster. Samples I-6, I-19, and PS showed signs of partial sintering, but this did not occur with TP. (At 880° C., porcelain crucibles were attacked, so that nickel crucibles had to be used instead.) The color changes proceeded more rapidly with finer materials. A pulverized (−100-mesh) sample became reddish brown after 2.5 hours' heating at 800° C., ap-

Table IV. Partial Analysis of Serpentine-Fused Phosphate Samples Used for Heat-Treatment Tests

	I-6	I-19	TP[a]	PS
	%	%	%	%
Total P₂O₅	23.24	21.77	20.3	20.37
Citric-sol. P₂O₅	13.32	21.05	18.5	19.56
Citric solubility	57.3	96.8	91.0	96.0
CaO	..	..	31.3	32.06
MgO	..	..	15.3	18.64
Fe₂O₃	..	..	3.2	2.51
Al₂O₃	..	..	3.0	2.29
F	..	..	1.5	..
SiO₂	..	..	24.7	23.70
Glass content	46.0	82.0	88.0	85.5

[a] Guaranteed analysis (18).

Table V. Effect of Heat Treatment on Citric Solubility and Glass Content of High- and Low-Grade Products

Sample No.	Size of sample	Treatment Received Maximum temp. reached, °C	Time of Heating at Max. Temp. Indicated Hr.	Min.	Rate of cooling	Citric Solubility[a], %	Glass Content, %
A-01[h]	−6-M[c]	800	2	30	Q[d]	10.5	21.0
A-02[h]	−40-M	800	2	30	Q	10.4	0.9
A-03[b]	−100-M	800	2	30	Q	14.1	1.7
A-04[e]	−6-M	810	1	10	SJ[f]	25.5	35.0
A-05[e]	−6-M	810	1	10	VS[g]	21.1	26.0
A-06[e]	−6-M	810	1	10	Q	25.4	34.0
A-07[h]	−6-M	840	4	0	Q	18.5	14.0
A-08[i]	−6-M	840	4	0	Q	33.8	10.0
A-09[j]	−6-M	840	4	0	Q	33.5	3.8
A-10[k]	−6-M	840	4	0	Q	17.3	10.0
I-19-A6	−20-M	500	4	0	Q	89.9	95.4
I-19-A7	−20-M	500	6	0	Q	92.0	91.0
I-19-A8	−20-M	500	8	0	Q	93.1	93.1
I-19-A14	−20-M	880	4	0	Q	29.4	24.0
I-19-A15	−20-M	880	6	0	Q	24.6	2.9
I-19-A16	−20-M	880	8	0	Q	29.8	1.8
TP-A6	−20-M	500	4	0	Q	95.0	83.5
TP-A7	−20-M	500	6	0	Q	86.5	88.5
TP-A8	−20-M	500	8	0	Q	93.6	77.5
TP-A14	−20-M	880	4	0	Q	47.5	1.8
TP-A15	−20-M	880	6	0	Q	47.3	1.0
TP-A16	−20-M	880	8	0	Q	40.2	0.9

[a] All determinations made on −100-mesh samples.
[b] High-grade sample with citric soly. of 93%; ground to fineness indicated.
[c] M stands for mesh.
[d] Quenching in water.
[e] Sample TP, cf. Table IV.
[f] Cooled slowly to room temperature.
[g] Cooled very slowly in muffle furnace.
[h, i, j, k] I-6, I-19, TP, and PS respectively; cf. Table IV.

pearing very much like a completely dehydrated Taiwan serpentine.

These physical changes were accompanied by simultaneous changes in phosphorus pentoxide solubility, which followed essentially the pattern previously reported (11).

Selected results of heat treatment tests as listed in Table V show that the intensity factor has a more decisive influence on solubility changes and different samples follow somewhat different patterns.

Observations under Polarizing Microscope A preliminary practice with apatites, phosphate rocks, raw serpentine, calcined serpentine, and serpentine- and olivine-fused phosphates was found to be very helpful. These materials were later used for daily reference.

To prepare a slide with a single-grained layer would be a good practice, but when only fine materials can be had this becomes impossible. The overlapping of glass and crystals was sometimes rather misleading. Occasionally, it was necessary to select the less densely packed fields for study.

Figure 3 illustrates how it is possible to estimate the relative abundance of glass and crystals.

With high-grade fused phosphates, only a few crystals could be identified, but occasionally a new field might in-

clude one or two large crystals. The reverse was true with reverted samples.

Assuming that the samples did not contain minerals of the isometric system such as periclase, rock salt, etc., the 10 estimations made for ea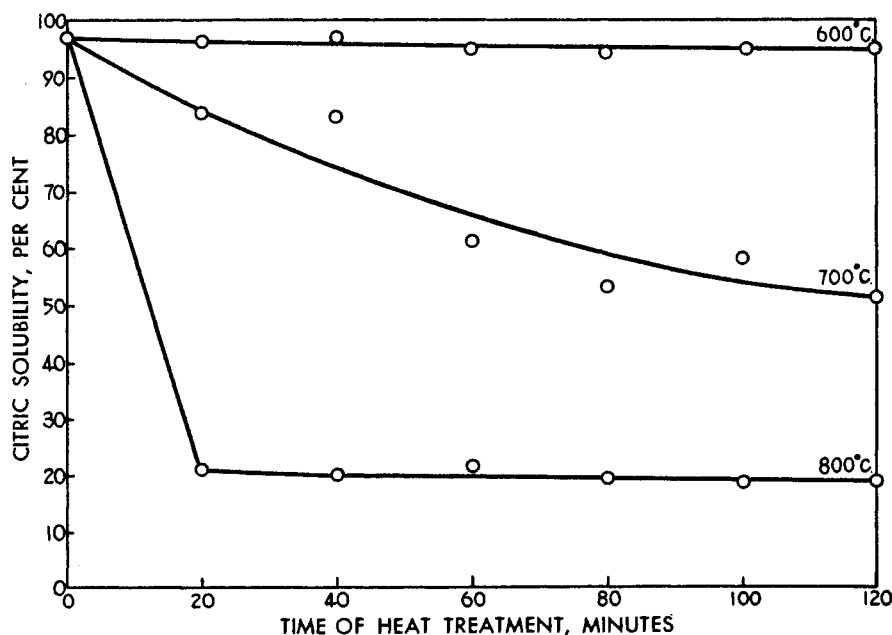ch sample gave the average glass content of each of the 165 samples. Some of the estimated results are shown in Tables I to VI.
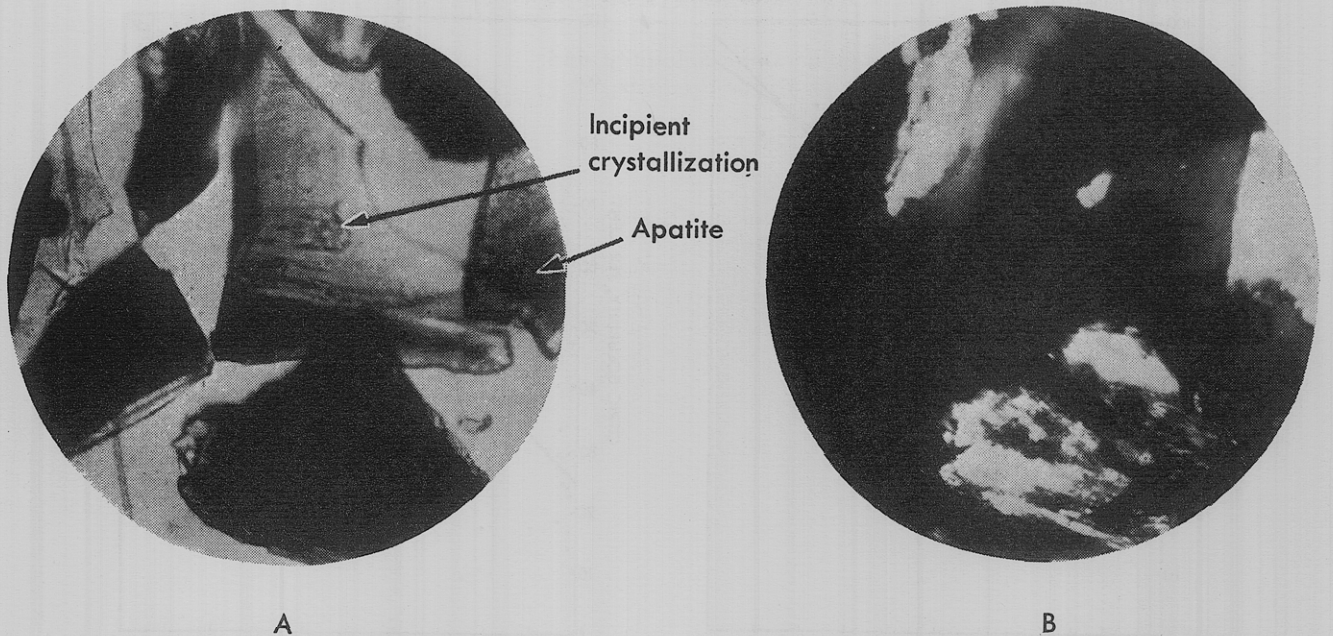
Transparent light green samples, such as PS, were full of clear light green glasses. The glasses of dark samples, such as those of the I and II series, ranged in color from reddish brown through brown to gray. Heat treatment increased the color of the glass. When heated at 700° C. for 2, 4, 6, and 8 hours, the glasses appeared translucent between crossed Nicol prisms and it became very difficult to decide which grain was amorphous and which was not, and much more difficult with smoky glasses such as those prepared from the Thermo-Phos Granular. Hence the heat-treated samples with the endings A9, A10, A11, and A12 are not considered in later correlation studies.

Apparently, completely reverted serpentine-fused phosphate should be made up substantially of apatite and minerals of the pyroxene group. In partly reverted samples, as apatite and pyroxene, minerals do not crystallize out simultaneously (7) and probably not at the same rate if they do, the amorphous portion left behind might change in composition and hence in solubility. High-grade serpentine-fused phosphate contained few crystals which might be neither apatite nor pyroxene, so that samples of different glass contents might incidentally have the same solubility.

Hill and associates report that low solubility of poorly quenched material is attributable to apatite formation (7). Apatite formation apparently was the main cause of most of the physical and chemical changes in the heat-treated samples shown in Table V. It is believed that the significant change in color of heat-treated samples (at 700° and

Figure 1. Effect of Heat Treatment on Solubility of Serpentine-Fused Phosphate

Figure 3. Photomicrographs of partly crystallized serpentine-fused phosphate ($\times$85)

A. Selected field of glass and crystals
B. Selected field of glass and crystals seen between crossed Nicol prisms.   total area on selected field occupied by glass and crystals
White areas are regions of crystallization which account for about 40% of   Incip. cryst. Incipient crystallization

880° C.) was due to the simultaneous formation of minerals of the pyroxene group.

Correlation Studies between Citric Solubility and Glass Content   A preliminary study of the results of the samples of the XS and LS series shows a close correlation between the citric solubility and the glass content of serpentine-fused phosphate (see Figure 4).

It is believed that the average relationship between the two variables might be expressed by a linear equation $Y =$ $a + bX$, in which Y and X stand for the citric solubility and the glass content, respectively. Based on the results of solubility tests and petrographical examinations for the 165 samples, applying the method of least squares, the following regression equation is obtained

$$Y = 24.7 + 0.750\,X \qquad (1)$$

The citric solubility is plotted against the glass content for the 165 samples in Figure 5. The curve showing the average relationship between the two variables is also plotted as shown.

Based on the average relationship as represented by Equation 1, it can be seen that on the average, the citric solubility of serpentine-fused phosphate would be equal to 99.7% for a glass content of 100% and equal to 24.7% for a completely reverted crystalline product. Hill and associates report that the citric solubility of Florida land-pebble and hard-rock phosphates varies from 17.2 to 27.4% (6) and that of Florida soft and waste-pond phosphates varies from 19.7 to 40.3% with an average of 28.7% for 24 samples (5). The average citric solubility of crystallized serpentine-fused phosphate is, therefore, no greater than that of untreated phosphate rock (3).

It can be seen in Figure 5 that only a few points fall on the regression curve. The correlation coefficient equals +0.895. Statistically, this is more than 99% confident for 165 pairs of determinations (2). Hence, it is concluded that the citric solubility of serpentine-fused phosphate is a function of its glass content.

It appears that the citric solubility of an unknown serpentine-fused phosphate sample might be measured indirectly by its glass content, based on the regression curve shown. The standard error of such an estimate equals 11.6%, which shows that the method is too inaccurate from the chemical point of view.

In Figure 5, the points representing the high-grade samples are congested at the upper right corner. It appears, therefore, that the curve might be used with confidence for screening undergrade products.

Sources of Error

In general, chemical determinations should be very accurate, if the prescribed

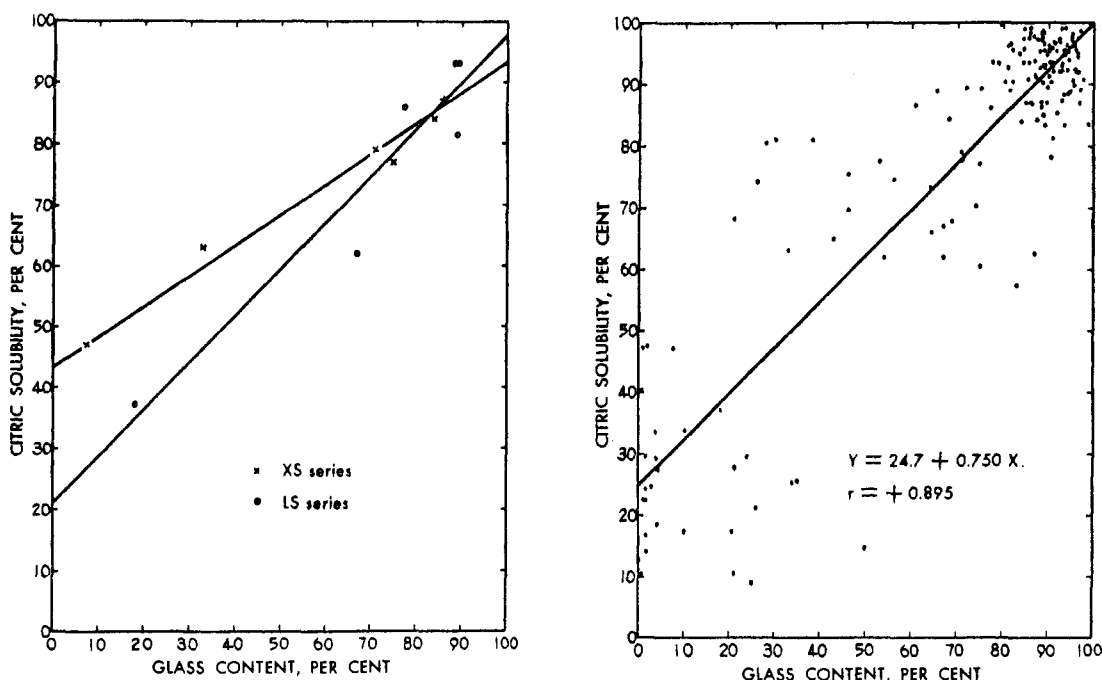Figure 2. Effect of Heat Treatment on Solubility of Serpentine-Fused Phosphate
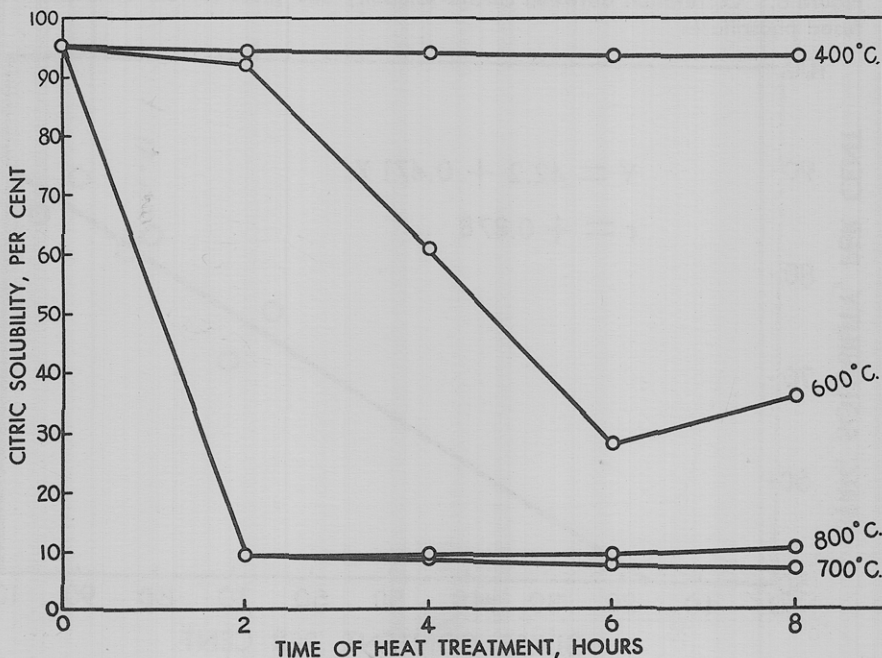
Figure 4. Relation between citric solubility and glass content of serpentine-fused phosphate samples. Figure 5. Correlation between citric solubility and glass content of amorphous and crystallized serpentine-fused phosphates

procedure is followed closely (1). However, as the coarse and fine fractions of serpentine-fused phosphate do not show the same solubility (11), samples should be taken carefully for best results. Regarding the glassy and crystalline nature of serpentine-fused phosphate:

Some observed crystals may have nothing to do with the $CaO-P_2O_5-MgO-SiO_2$ system.

Phosphatic and nonphosphatic constituents may not crystallize out simultaneously (7); hence crystallization may not affect to the same extent the chemical solubility of the residual glass, and moreover, crystals are themselves somewhat soluble.

Glass may be adhered to, embedded in, or sprinkled with difficultly soluble crystals (7).

Soluble glass may be coated with a layer of difficultly soluble glass—e. g., siliceous.

While crystallization is in progress, with some smoky samples, it is sometimes rather difficult to decide whether a translucent grain should be considered amorphous, crystalline, or otherwise.

The grains or fragments of either glasses or crystals are three-dimensional, so that the accuracy of estimations based on a two-dimensional concept is limited.

Some samples are contaminated with metallic materials which do not transmit light.

Observations based on a sample weighing less than 0.1 gram can never be as reliable as the results of chemical analysis made on a 5.0-gram sample (7), except for all-amorphous or completely crystallized samples.

These considerations explain why the 165 points do not fall on the same straight line and why the standard error of estimate is as high as 11.6%.

Chemically speaking, olivine-fused phosphate does not differ much from serpentine-fused phosphate (7), except

that the former usually has a slightly higher phosphorus pentoxide content. It is believed that the above discussions may apply equally well to olivine-fused phosphate.

Both 2% citric acid and neutral ammonium citrate have been used for measuring the solubility of serpentine- and olivine-fused phosphates. Hill and associates report that the citric acid test usually gives higher results with coarse materials, whereas the citrate test is more sensitive to fineness; with some samples, both tests give comparable results (4, 7).

The above discussions indicate that the citrate solubility of serpentine-fused phosphate also varies as the glass content.
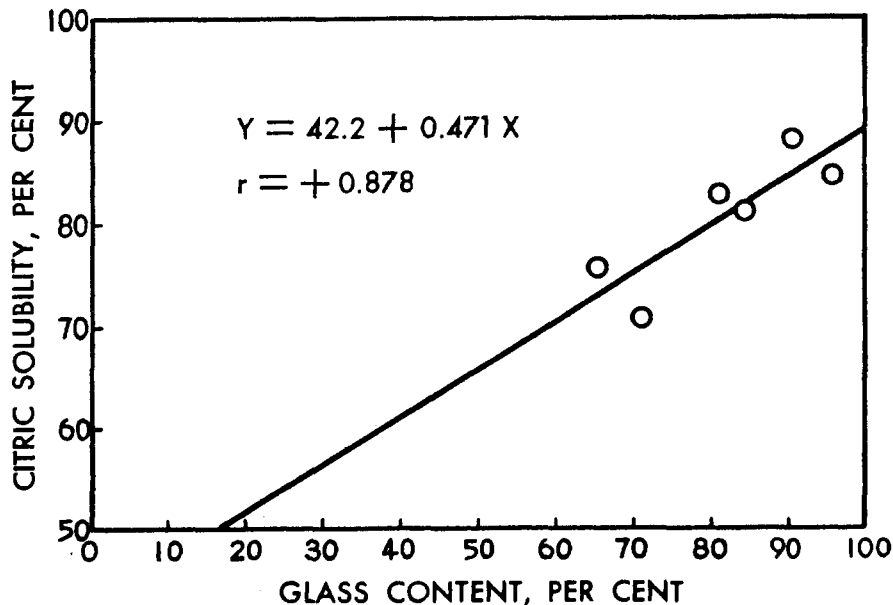
That this is true can be seen from Table VI and Figure 6.

Table VI. Citric Solubility, Citrate Solubility, and Glass Content of Some High- and Low-Grade Products

Sample No.	Citric Solubility[a], %	Citrate Solubility[a], %	Glass Content, %
II-18	89.0	75.5	65.5
I-23-S1	77.8	70.8	71.0
II-25	96.2	82.8	81.0
II-19	95.9	81.3	84.5
PS-1	96.0	88.1	90.8
M-100	92.3	84.7	95.8

[a] All determinations made on −100-mesh samples.

Figure 6. Correlation between citrate solubility and glass content of serpentine-fused phosphates

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LIMING MATERIALS IN SOILS

Radiochemical Measurement of Reaction Rates

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This investigation was intended to demonstrate the usefulness of radiocalcium in evaluating
liming materials, and to develop a radiochemical method applicable to the study of nat-
ural materials, yet subject to fewer obvious errors than those associated with commonly
used techniques. It was found that reaction rates of liming materials could be followed
by tagging the calcium of the exchange complex of a soil, incorporating the liming ma-
terial, and determining the specific activity of the calcium in successive crops grown on the
system. A second successful method involved measurement of calcium-45 and calcium-40
concentrations in dilute calcium nitrate solution before and after equilibration with a
sample of soil previously treated with limestone or slag. The methods developed provide
a more direct means of evaluating limestones and slags than was previously available.
The equilibration technique shows promise as a means of determining exchangeable cal-
cium, and should be particularly valuable when applied to calcareous soils or those con-
taining residual limestone.

THE EFFECTIVENESS of a limestone
or slag as a soil amendment de-
pends mainly upon two properties of
the material: its potential capacity to
neutralize soil acidity, and the rate at
which the material will react in the soil
to accomplish the neutralization.

Of these properties, the reaction rate
is the more difficult to measure. No one
of the numerous methods that have been
developed for its determination is en-
tirely satisfactory. In greenhouse or
field experiments, some of the measure-
ments involved are questionable. Soil
pH is subject to natural fluctuations over